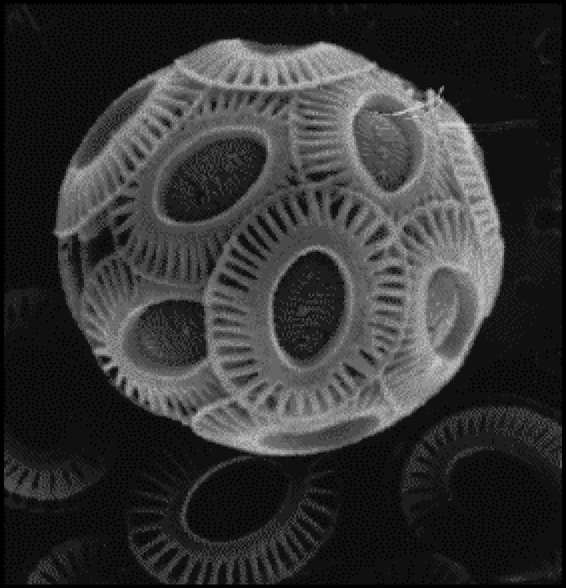
Calcium Carbonate Budgets
- the Basic Framework -*

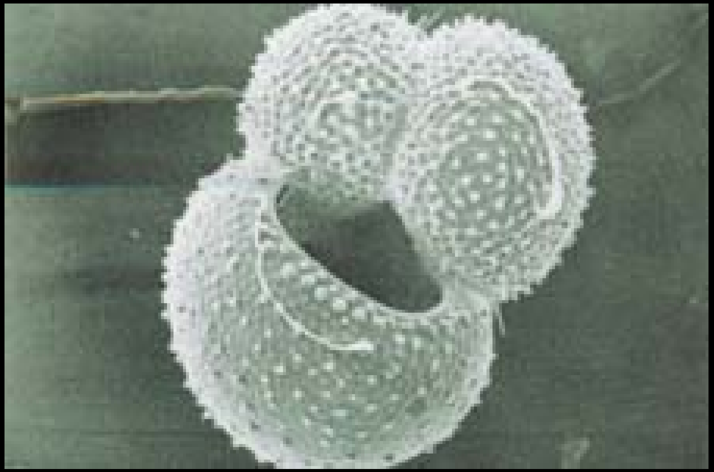
*title provided by Jim Hendee

Coccolithophores
calcite



T. Tyrrel

Forams
calcite

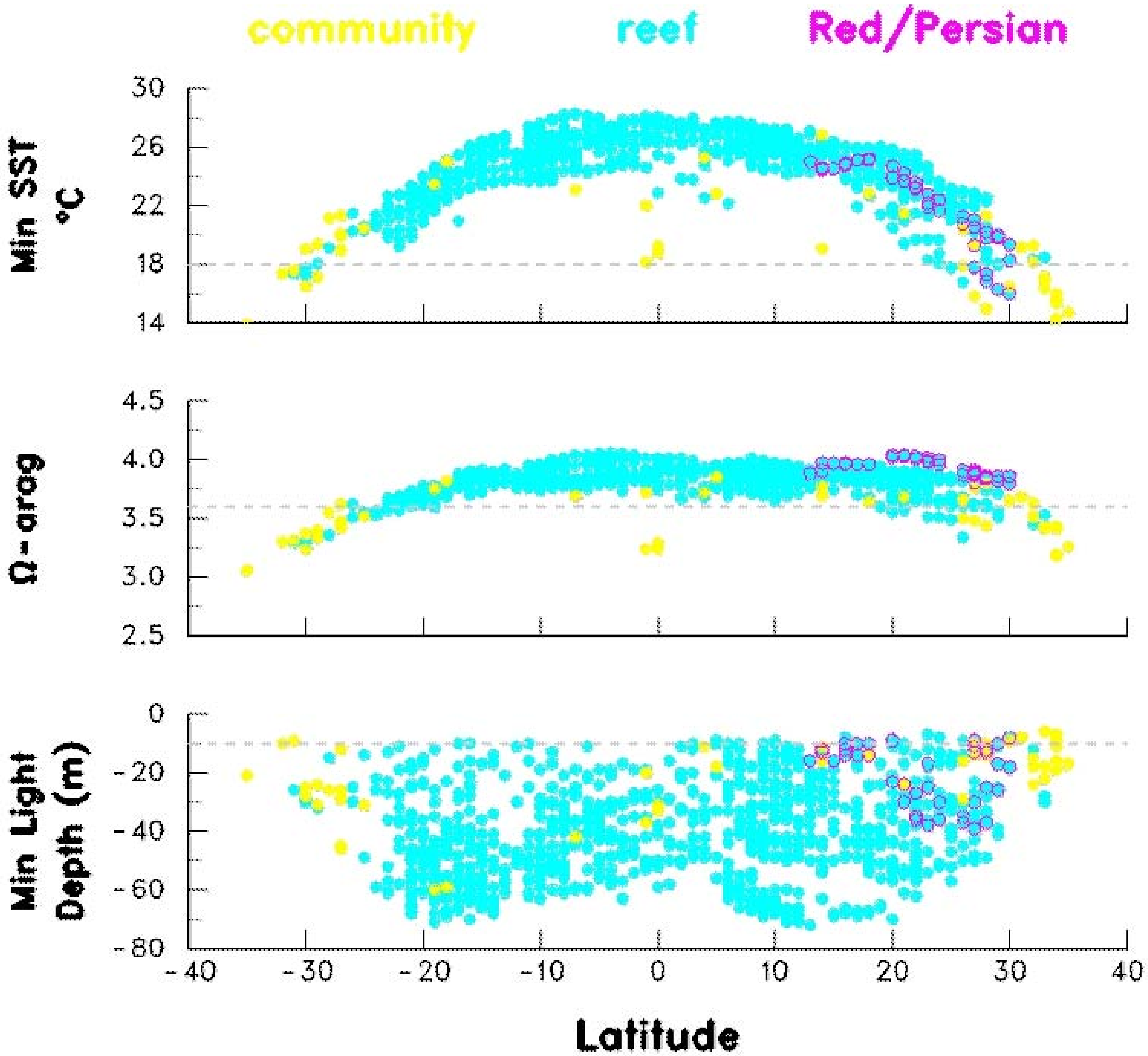


Calcareous algae
High-Mg calcite

Nancy Sefton

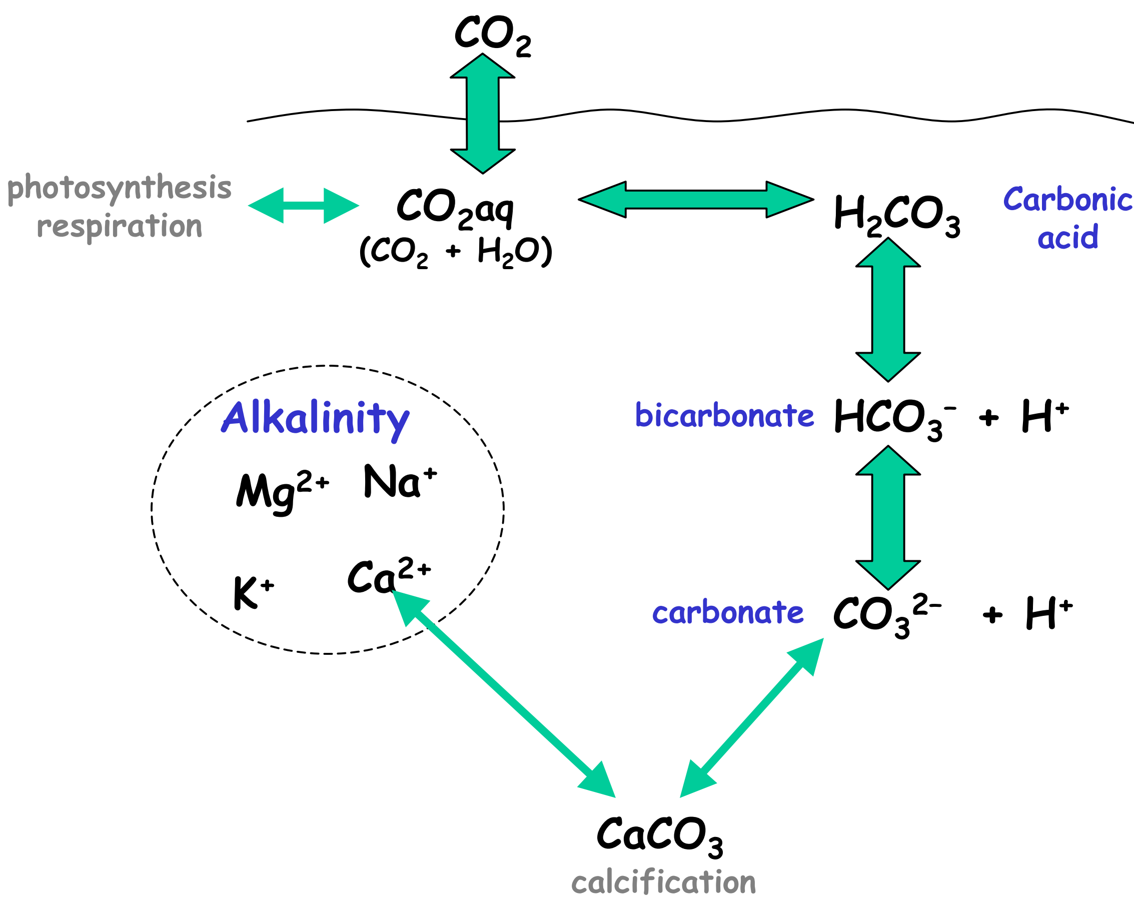
Corals
aragonite

NOAA



community
reef
Red/Persian
Min SST °C
30
26
22
18
14
Ω-arag
4.5
4.0
3.5
3.0
2.5
Min Light Depth (m)
0
-20
-40
-60
-80
-40
-30
-20
-10
0
10
20
30
40
Latitude

Carbonate Chemistry

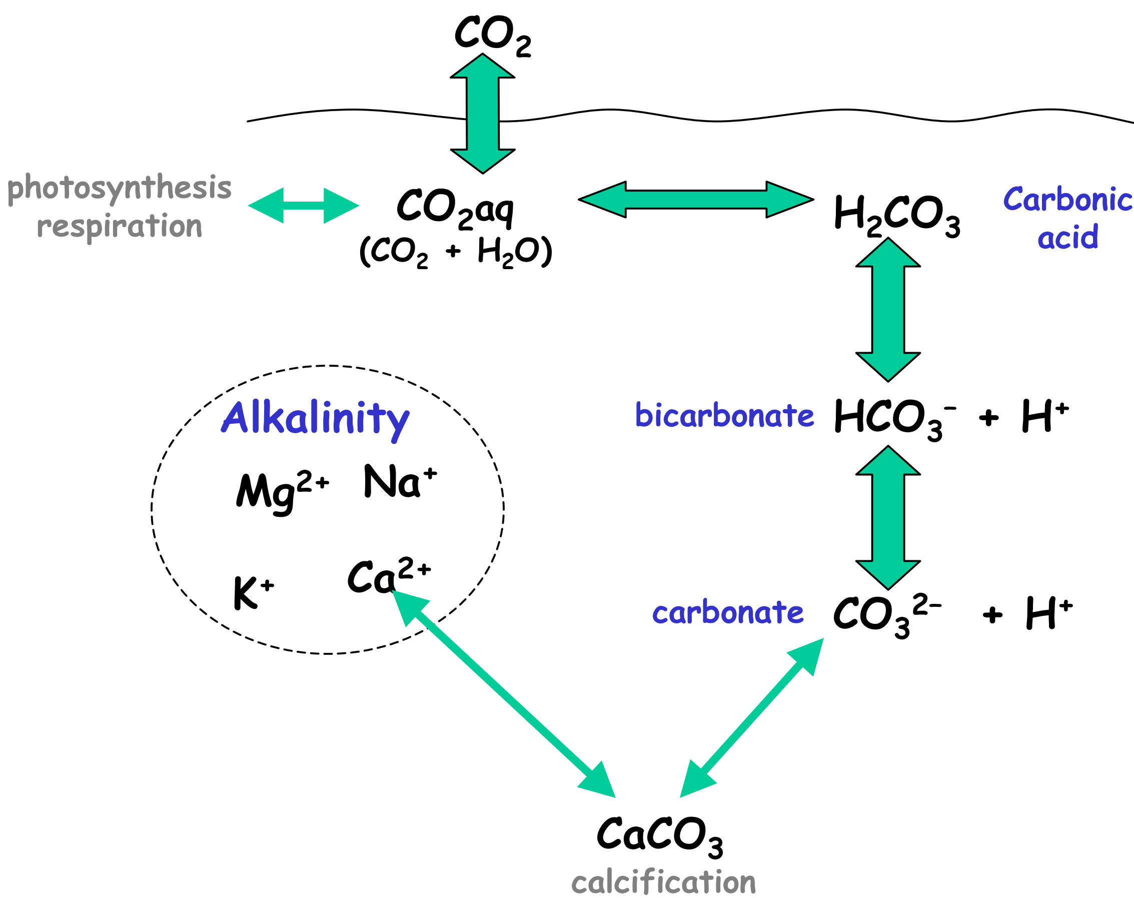


Proportions of HCO_3^- and CO_3^{2-} adjust to balance alkalinity

$$[CO_3^{2-}] = ALK - \sum CO_2$$

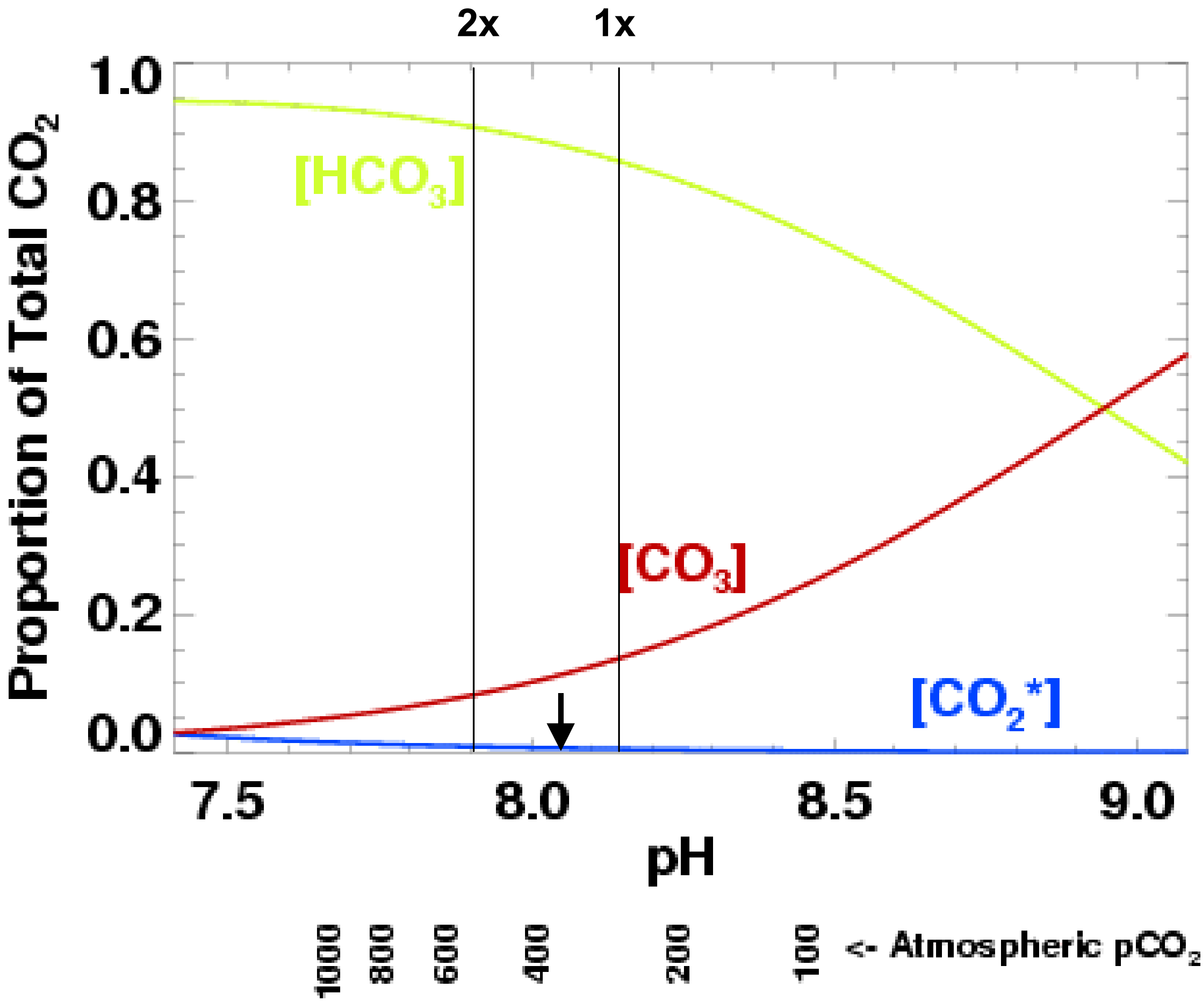
$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp}$$

Carbonate Chemistry

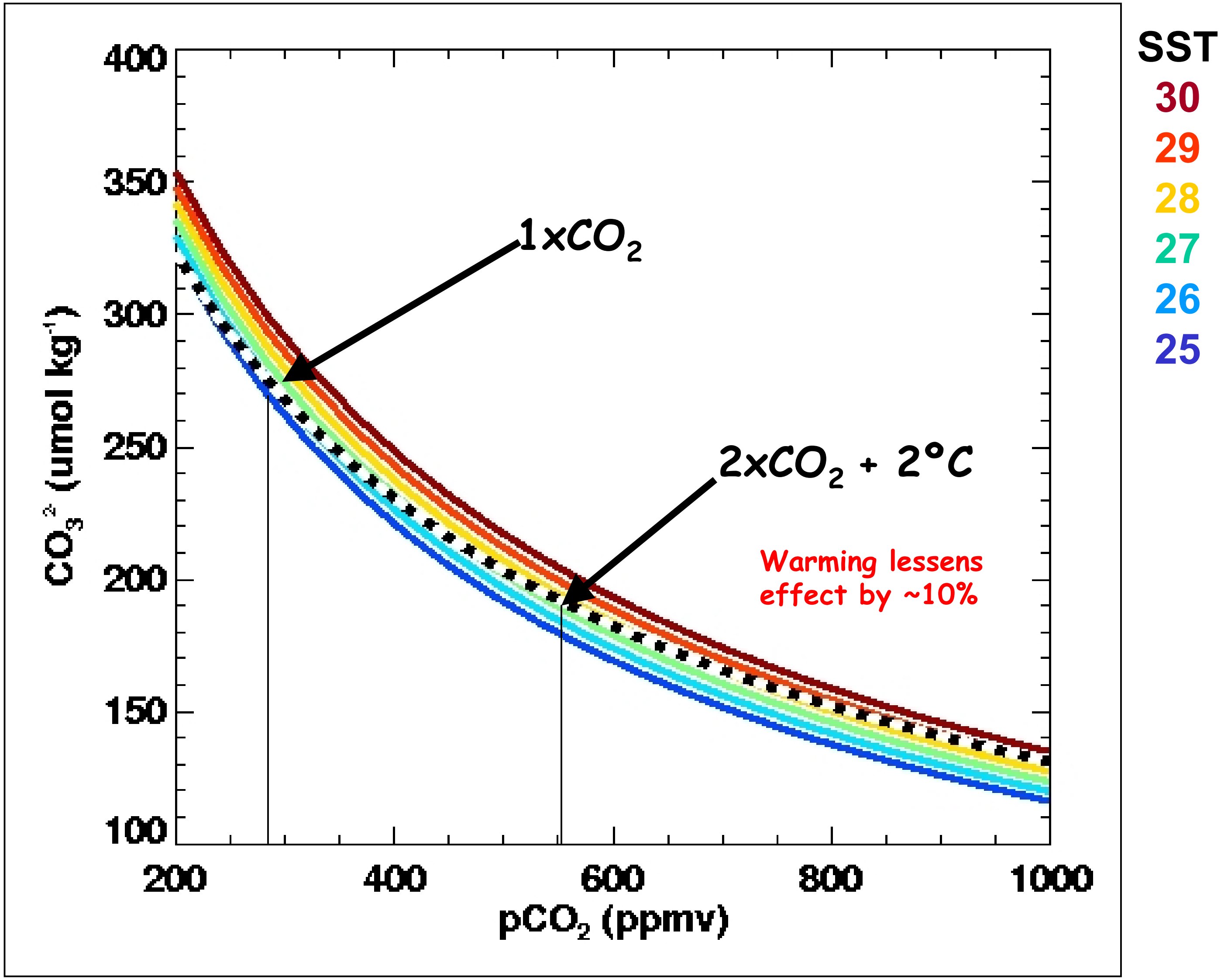


$1xCO_2$	$2xCO_2$	
280	560	
8	16	
1635	1867	
272	177	
1915	2061	TCO_2
8.17	7.93	pH
4.3	2.8	Ω-arag

Proportion of Carbonate Species

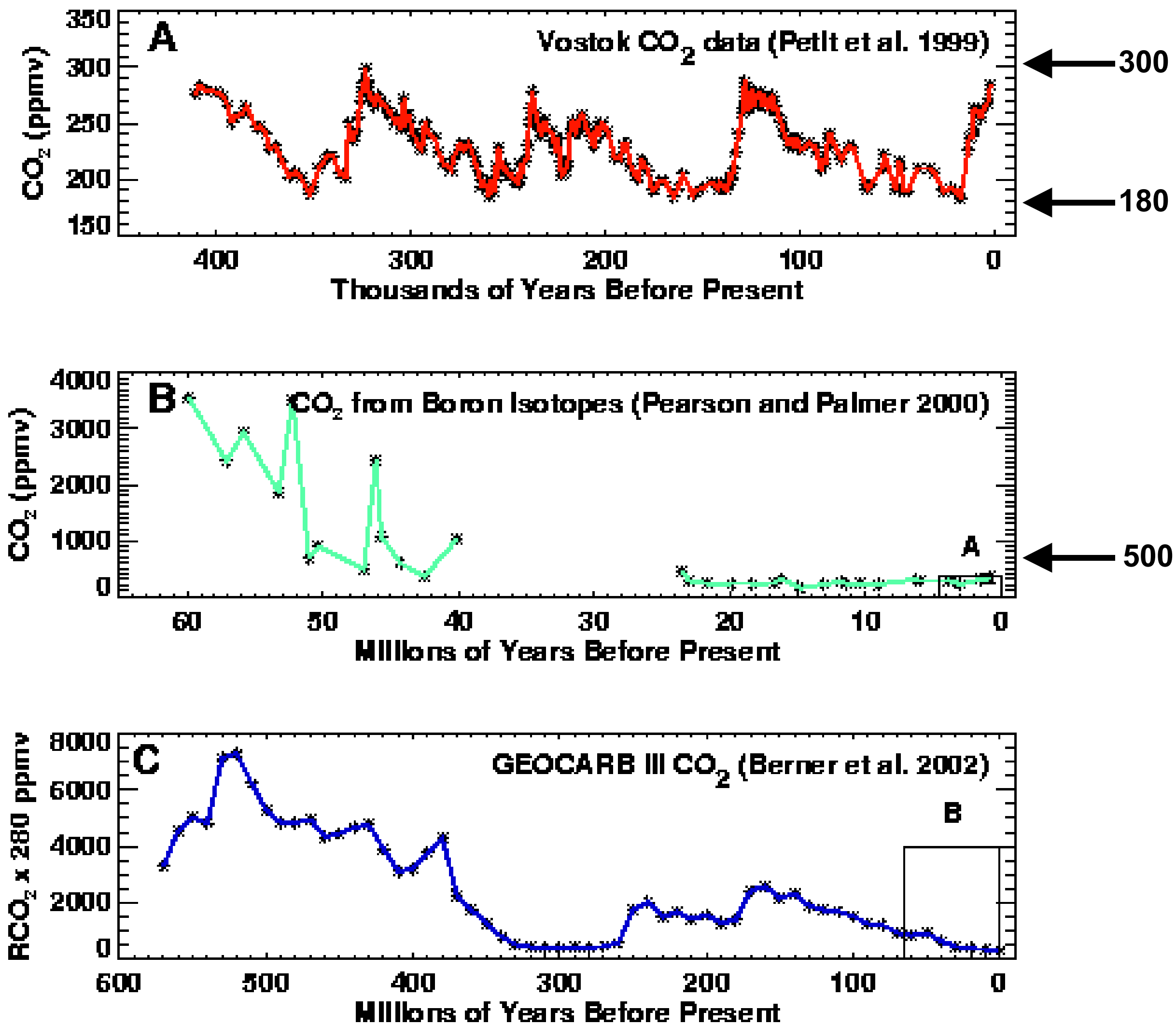


Effect of Temperature on $[CO_3^{2-}]$

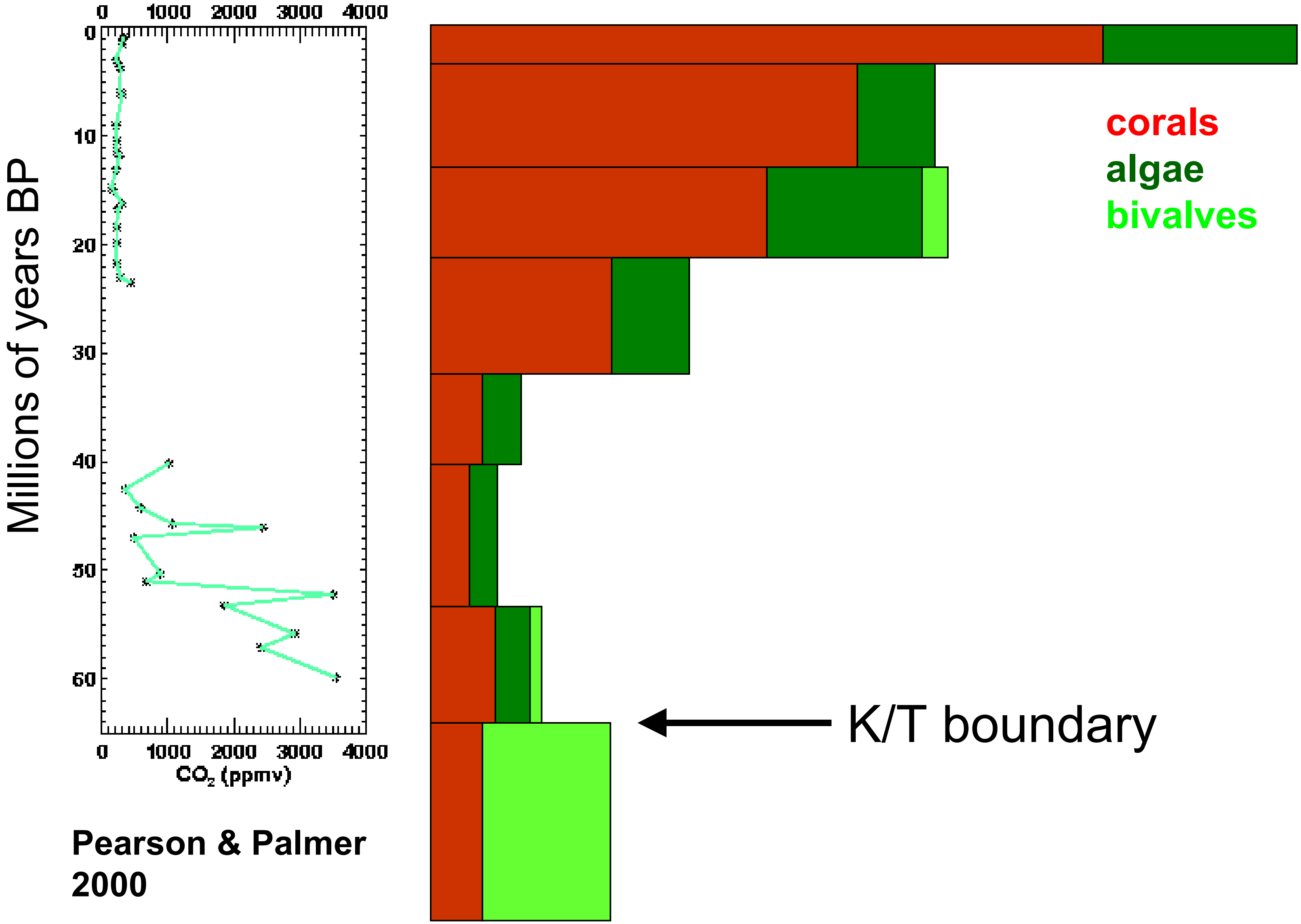


Records of Past Atmospheric CO_2

Latest lines of evidence suggest that CO_2 levels have been below 500 ppmv since the Miocene (~24 my ago)



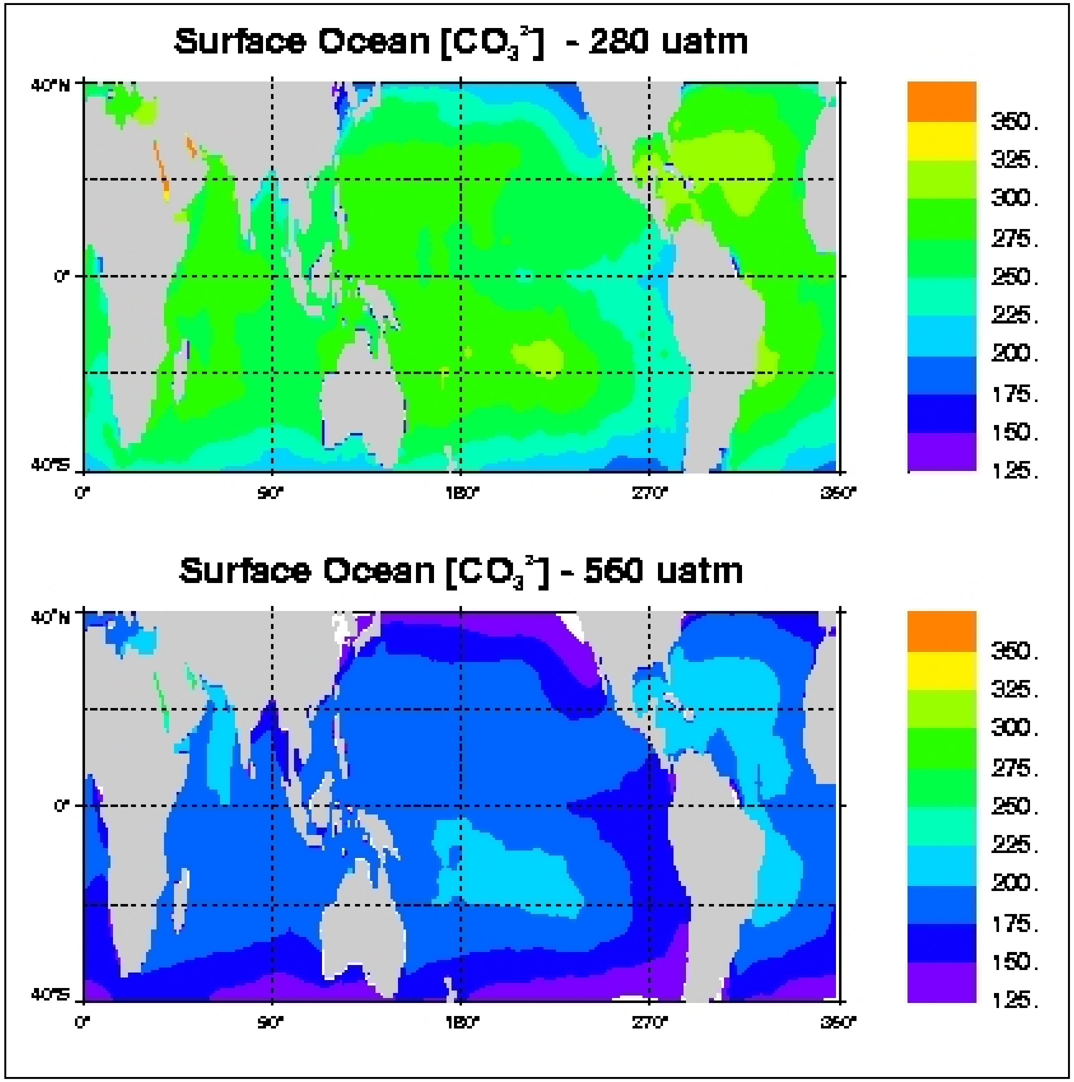
Coral/algal reef development over time



Pearson & Palmer 2000

Kiessling et al. 1999

[CO_3^{2-}] at 280 ppmv and 560 ppmv



Coral versus Reef Calcification

CORALS ***biology/ecology***

- Lower calcification means weaker and/or slower growing corals?
- Less competitive for space on reef?
- More susceptible to damage

REEFS ***geology***

- Lower $CaCO_3$ production/cementation
- Higher $CaCO_3$ dissolution
- Reef $CaCO_3$ budget reduced
- Loss of reefs, atolls, coral cays

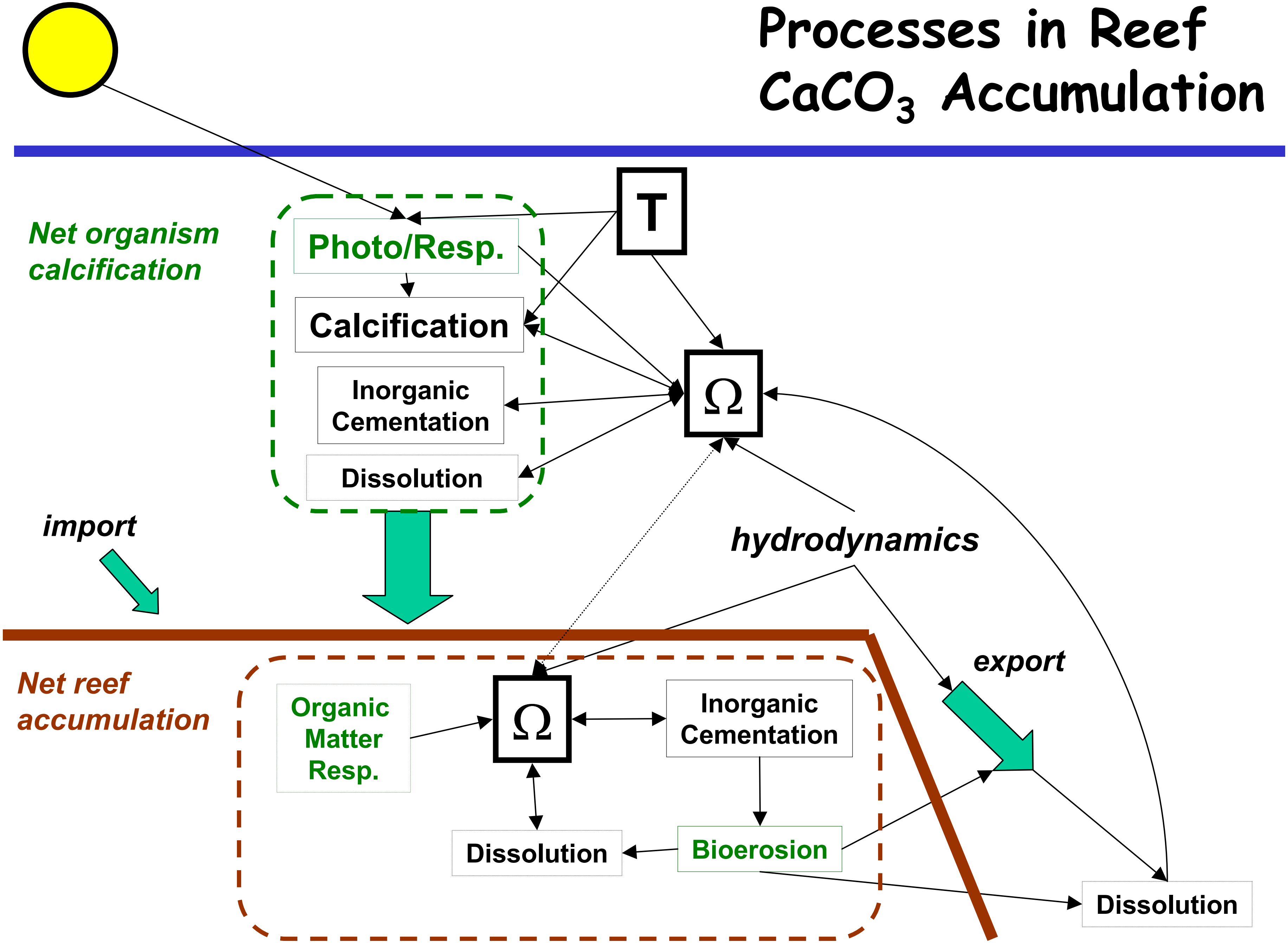
Other Ecosystems

Estimates of present-day carbonate flux, production & accumulation

from Milliman & Droxler 1996

Habitat	Area x10^6 km^2	$CaCO_3$ flux $g/m^2/y$	$CaCO_3$ prod. 10^{12} mol/y	$CaCO_3$ accum. 10^{12} mol/y
reefs	0.6	1500	9	7
banks	0.8	500	4	2
carbonate shelves	10.0	20-100	6	3
open ocean	290.0	20	60	11

Processes in Reef $CaCO_3$ Accumulation



Calcification Measurements
(not always the same thing)

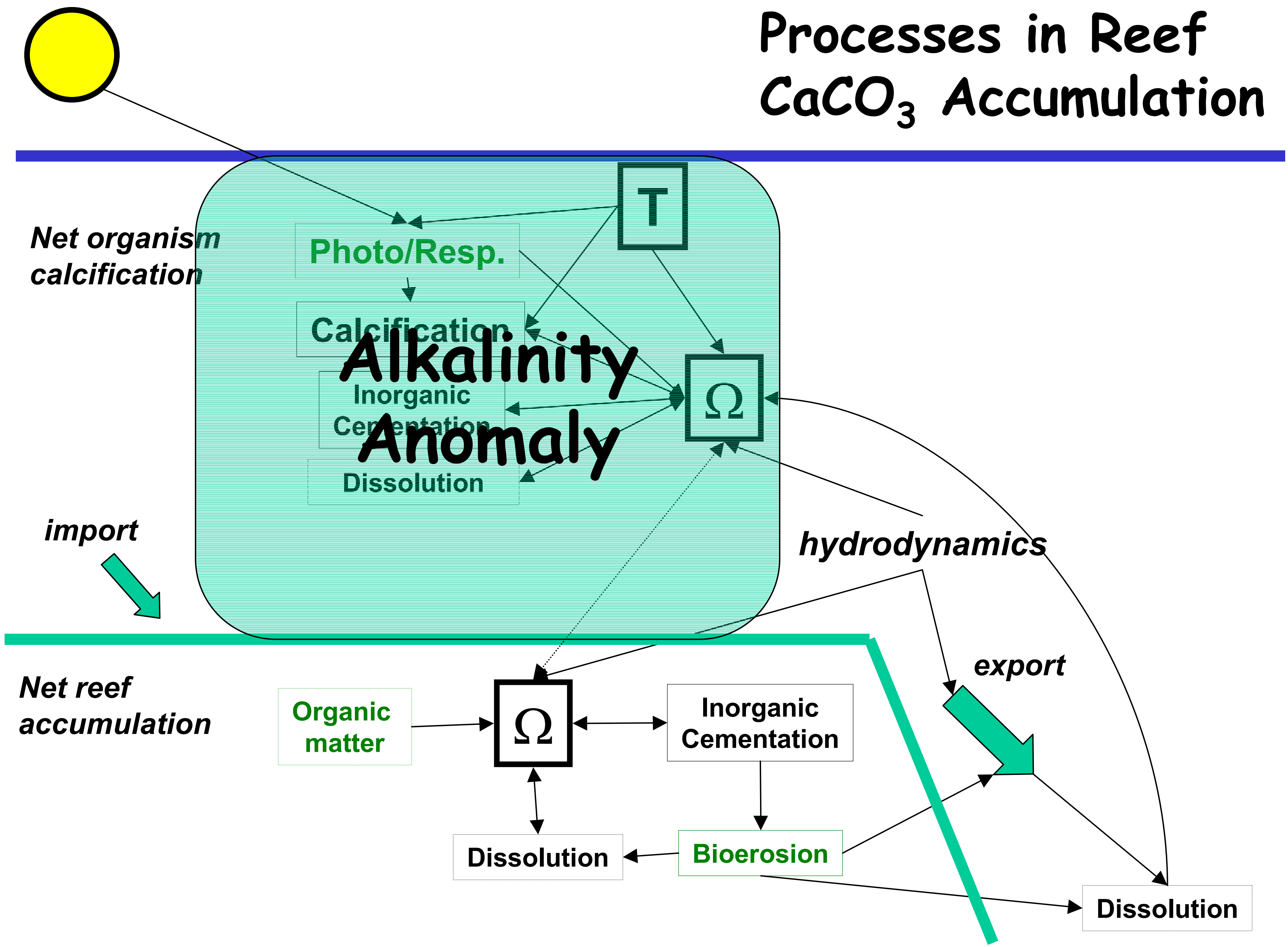
Technique	Measures:	Timescale
Buoyant weight	$G_{skel} + D_{skel}$	Duration of experiment
? Alk of monoculture	$G_{skel} + D_{skel}$	Discrete measurements over duration of experiment
Coral band increment	$G_{skel} + D_{skel} + G_{inorg}$	Integrated over time of band formation + post-depositional cementation
? Alk of closed system	$G_{sys} + D_{sys}$	Discrete measurements over duration of experiment
? Alk in open system	$G_{sys} + D_{sys}$ + mixing	Discrete measurements over duration of experiment – requires knowledge of mixing regime

Biogenic Calcification
(individual species)

Species	Extension rate cm y^{-1}	G* g $CaCO_3$ cm^{-2} y^{-1}	source
F pallida	0.41-0.71 (0.57)	0.59-1.32 (0.82)	Highsmith 1979
G retiformis	0.49-0.85 (0.68)	0.83-1.45 (1.16)	Highsmith 1979
P lutea	0.35-1.18 (0.76)	0.49-1.66 (1.07)	Highsmith 1979
M annularis	0.61-1.44 (0.98)	0.77-1.55 (1.23)	Dodge & Brass 1984
Porites spp.	0.13-2.21 (1.25)	0.51-2.81 (1.60)	Lough et al. 1999
P lutea	0.61-1.69 (1.09)	0.66-1.96 (1.25)	Bessat & Bigues 2001
Coral species (alk anomaly)	-	?	?
Coralline algae	-	?	?
Inorganic cementation	-	?	Enmar et al. 2000
Skeletal dissolution	-	?	?

* G is per surface area of the organism

Processes in Reef $CaCO_3$ Accumulation



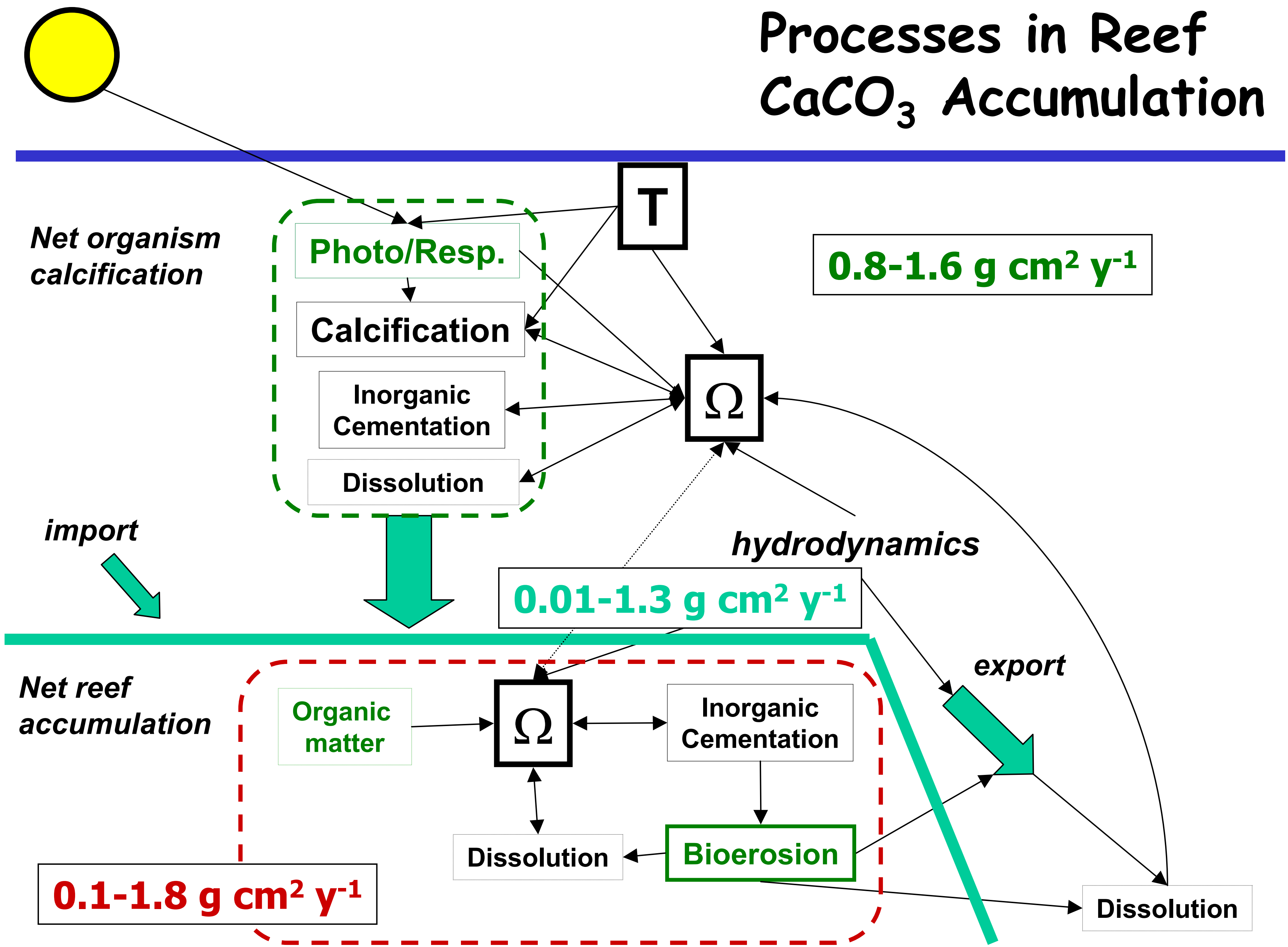
Coral Community & Reef Calcification

System	G* g $CaCO_3$ cm^{-2} y^{-1}	Source
Mesocosm	0.53	Leclerc et al. 2002
B2 mesocosm	0.27	Langdon et al. 2000
REEFS** Reef flats Algal-dominated Sediments	 0.05-1.26 -0.004-0.40 -0.01-0.12	Reviewed by Gattuso et al. 1998
Halimeda meadows	0.01-0.24	Freile & Hillis 1998
Inorganic cementation**	$1x10^{-4}$ g cm^{-3} y^{-1}	Buddemeier & Oberdorfer 1986
Reef accumulation from cores (50% porosity)	0.12-1.80 0.84 (modal value)	Hopley & Davies (submitted)
Dissolution	?	Halley & Yates 2000 Chisholm & Barnes

*G is per surface area of the reef

**Measurements are usually restricted to closed, shallow water systems

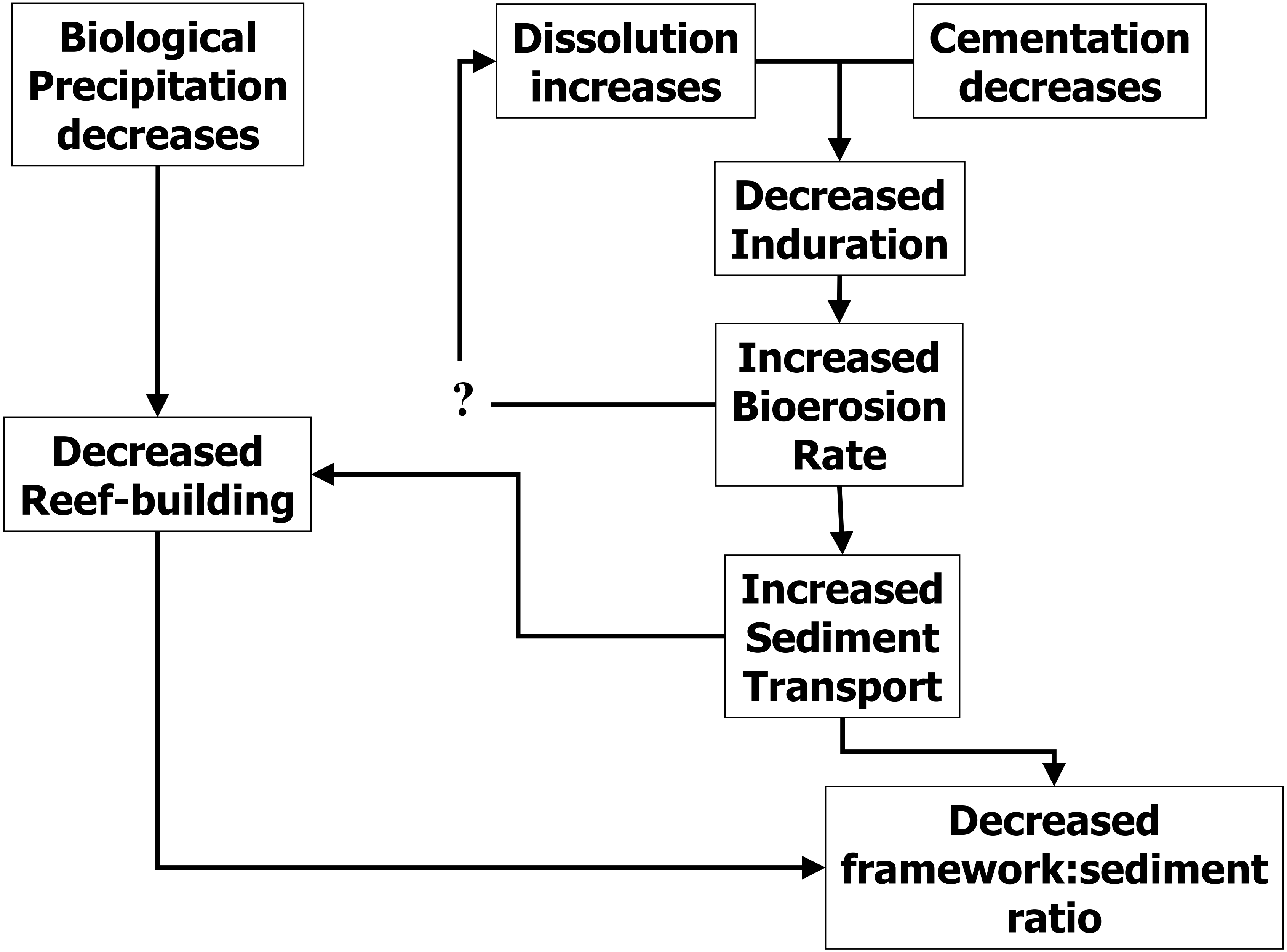
Processes in Reef $CaCO_3$ Accumulation



Bioerosion Rates*

Location & substrate	Bioerosion g $CaCO_3$ cm^{-3} y^{-1}	Source
Moorea *Hydrolithon onkodes*	0.12 (live) 0.49 (dead)	
Reunion & Moorea reef flats	0.8 (max)	Peyrot-Clausade et al. 2000
French Polynesia lagoons (*Porites lutea* blocks)	0.25 (max)	Pari et al. 1998
Kenya reefs (based on echinoid gut contents)	0.120 (unprotected) 0.005 (protected) 0.071 (newly protected)	Carreiro-Silva & McClanahan 2001
Lee Stocking I & One Tree I (microbial bioerosion only)	0.052 (LSI leeward reef) 0.0001 (LSI 275 m) 0.002 (OTI patch reef)	Vogel et al. 2000
Galápagos (blocks of *P lobata* and cathedral limestone)	2.54 (*P lobata*) 0.26 int + 2.28 ext 0.41 (cathedral ls) 0.06 int + 0.35 ext	Reaka-Kudla et al. 1996

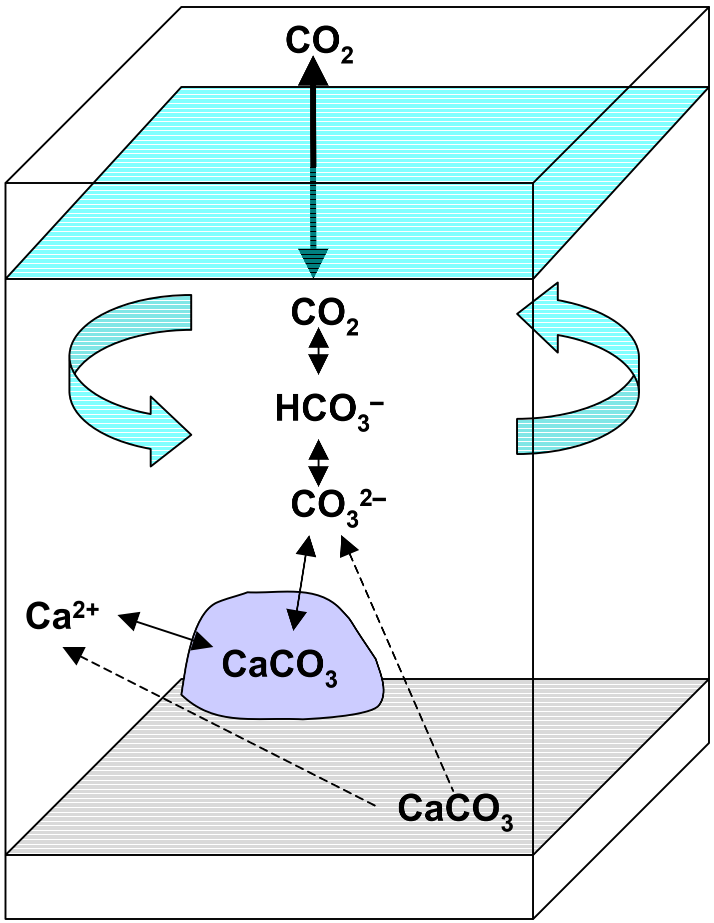
* Values are difficult to interpret in terms of net calcification (Bioerosion ≠ dissolution)
Important <u>process</u>
Need to differentiate chemical and mechanical components


Biological Precipitation decreases
Dissolution increases
Cementation decreases
Decreased Induration
Increased Bioerosion Rate
?
Decreased Reef-building
Increased Sediment Transport
Decreased framework:sediment ratio

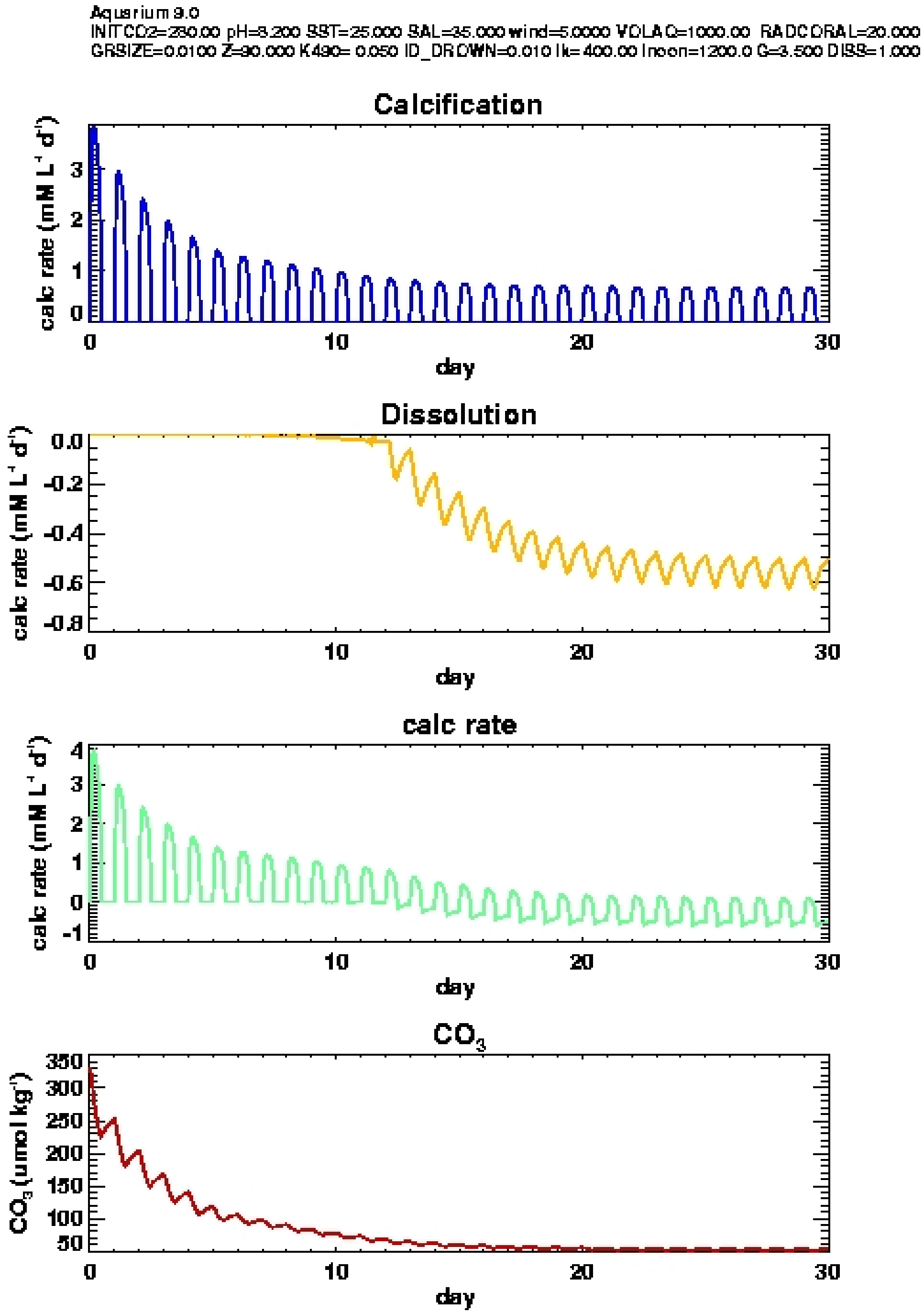
Closed system processes

Typical aquarium (closed) system

- coral (calcifying surface)
- sediments (mineral composition, grain size)
- water volume, well mixed, open to air-sea gas exchange
- diurnal light cycle



- calcification
  f(I, $CaCO_3$ saturation state)
- sediment dissolution
  f($CaCO_3$ saturation state)
- air-sea gas exchange f(T, wind speed, air-sea pCO_2 gradient)
- changes in seawater chemistry are calculated



Closed system results

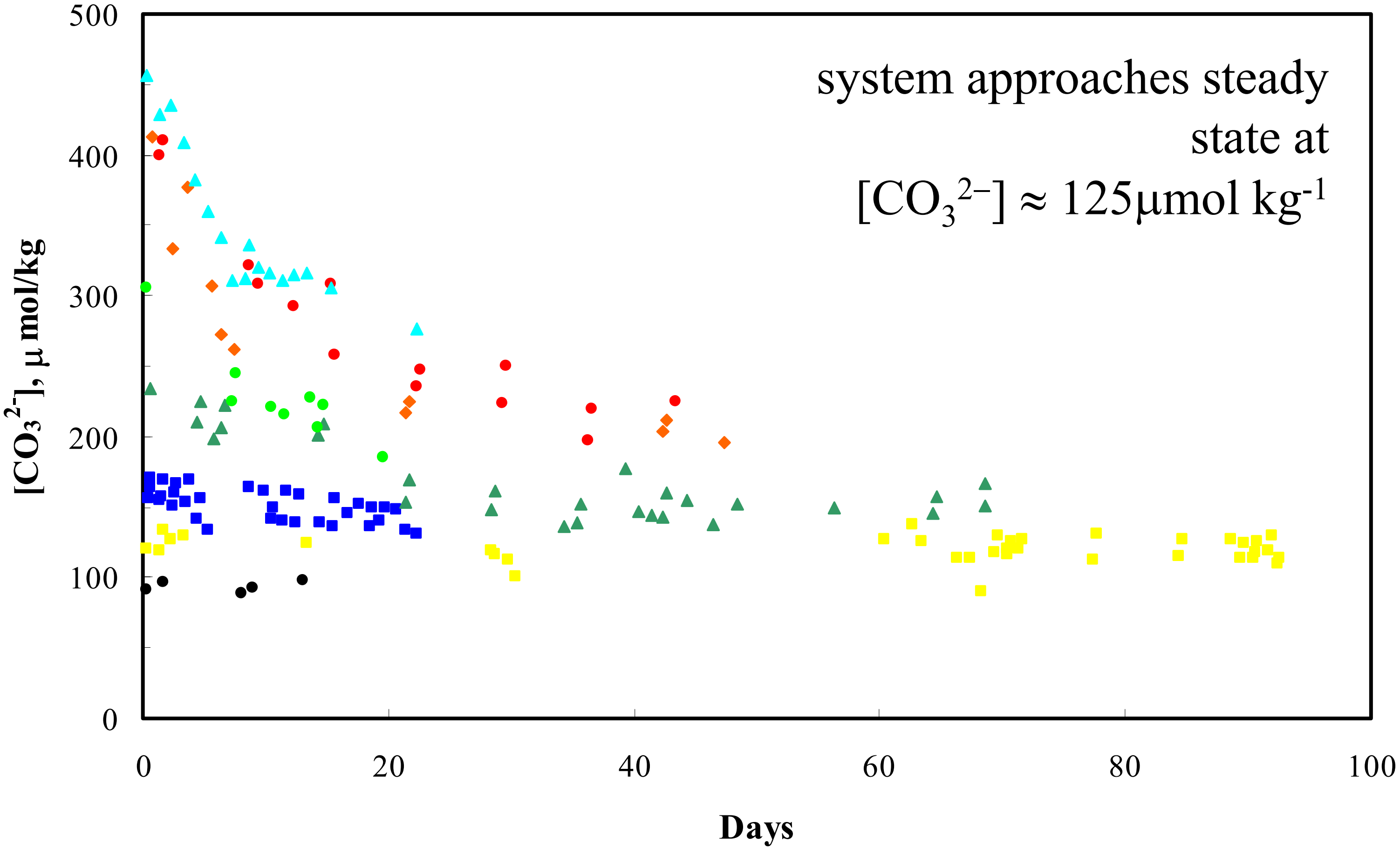
Diurnal cycle of calcification progressively alters seawater chemistry

Dissolution kicks in once saturation state drops below that of high magnesium calcite

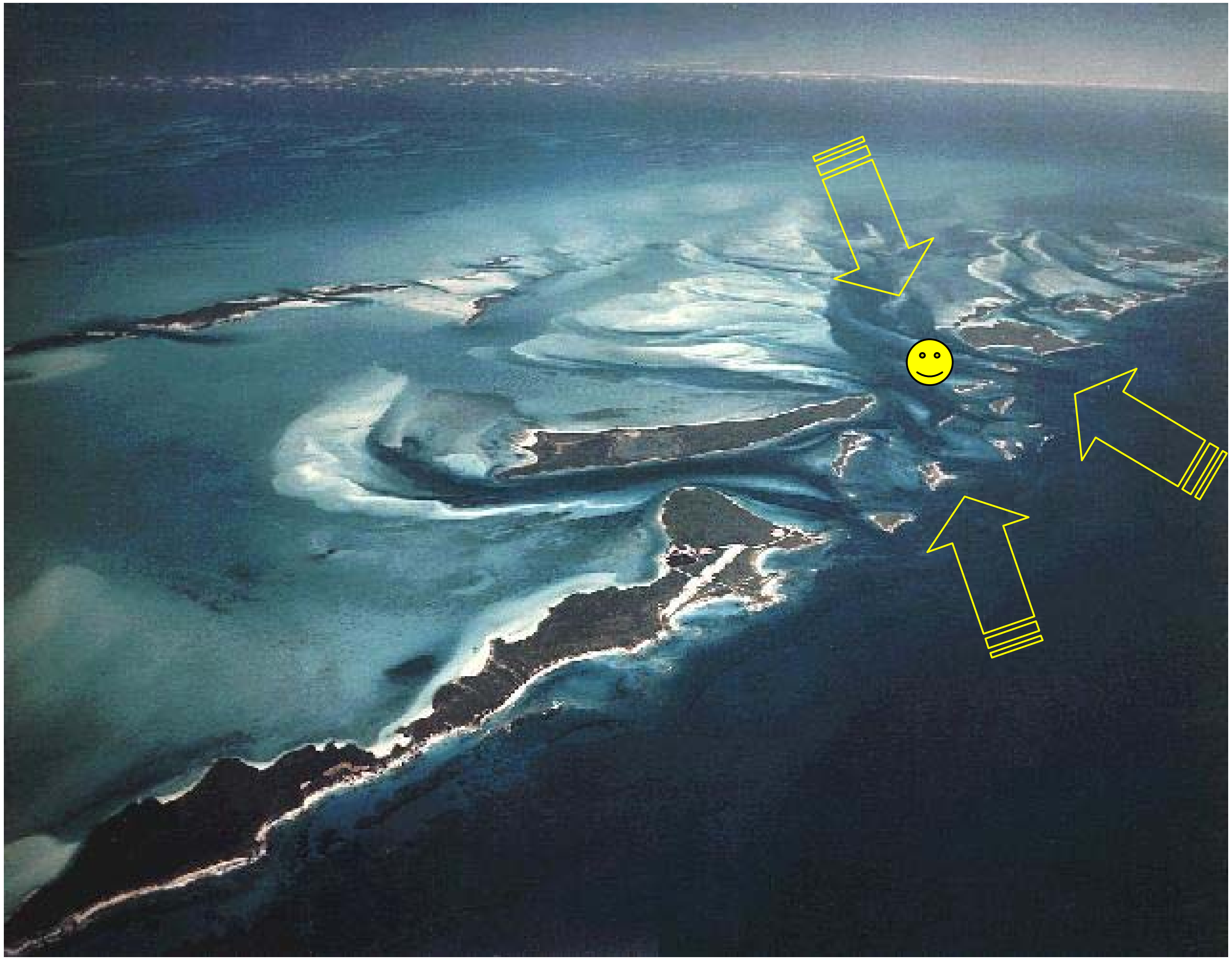
Net calcification

System approaches steady state after about 10-20 days

$[CO_3^{2-}]$ in Biosphere2 Mesocosm



C.Langdon, ICRS 2000



Conclusions

1. $CaCO_3$ budgets are only poorly quantified

2. $CaCO_3$ budgets will almost certainly change
   - $CaCO_3$ production will go down
   - $CaCO_3$ dissolution will increase
   - Bioerosion likely to increase

3. Need for field-validation of CO_2 effects on reef seawater chemistry and organisms

4. Questions: Coral communities are necessary to build reefs – are reefs necessary for coral communities?

5. Calcareous algae???

Shifts in Coral Reef Publication Topics